

SHALLOW PHOSPHOROUS DIFFUSION IN SILICON

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CERTIFICATE

This is to certify that the thesis entitled  
"Shallow Phosphorous Diffusion in Silicon" by D.R. Mohan  
Rao is a record of work carried out under my supervision  
and has not been submitted elsewhere for a degree.

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### ABSTRACT

Shallow Phosphorous diffusion into p-type silicon was done, resulting in junction situated close to the surface. Diffusions were done at temperatures ranging from 850°C to 1060°C. Junction depths varied from 0.5 micron to 2 microns. Impurity profile for each diffusion was evaluated employing anodic oxidation of silicon. The validity of moving boundary solution of Fick's second law was verified and the diffusion constants of phosphorous were calculated.

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### LIST OF SYMBOLS

$C(x, t)$	-	Total Phosphorous Concentration at distance $x$ from the surface for a diffusion time. $t$ .
$C_A(x, t)$ & $C_B(x, t)$	-	Concentration of the species A and B at $x$ and for a diffusion time $t$ .
$C_s$	-	Surface concentration of phosphorous
$C_B(x_0)$	-	Concentration of the B species at the phase boundary $x_0$ .
$D_A$ and $D_B$	-	Diffusion constants of A and B species of phosphorous.
$e$	-	electronic charge.
$K$	-	$C_B(x_0)/C_s$
$\alpha$	-	rate constant defined by $x_0 = \alpha t$ .
$\sigma$	-	Bulk conductivity of the sample
$\rho$	-	Bulk resistivity of the sample
$\sigma_s$	-	Sheet conductance of the sample
$\rho_s$	-	Sheet resistance of the sample

## INTRODUCTION

Diffusion of acceptor and donor type impurities into silicon is a basic step in the fabrication of integrated circuits. A monolithic circuit can be arrived at by following any one of the three basic processes (i) epitaxial-diffused process (ii) diffused-collector process and (iii) the triple diffusion process and in all these three, no matter what be the particular process followed, multiple diffusion of impurities is inevitable. As the performance of the individual components in the chip and the isolation achieved by the diffusion when it is used for that (for eg in epitaxial diffusion process and triple diffusion process) are of extreme importance in the final product<sup>1</sup>, the process of diffusion assumes an all important role in device fabrication.

Once impurities are diffused into silicon wafer, to form junctions, immediate thing one tries to find out is, how these impurities are distributed inside. This important investigation serves two purposes.

If one can characterise the distribution as following a particular law during diffusion, any other time, given some known or assumed conditions the unknown parameters of the system can be predicted. For example, if the distribution exactly is error function like, for some required

junction depth one can find out how much time the source of impurities must be on, for other known parameters like temperature background doping diffusion constant etc., So this necessitates the mathematical formulation of the problem, which gives out as a solution the expected distribution of impurities under the given conditions. Obviously this theoretical formulation must be experimentally proved to arrive at correct predictions and so the necessity of evaluating the profile of impurities and comparing that with theoretical values, point by point, arises. This will be one aspect of the investigation.

The other one is of design consideration.

Knowledge of the concentrations and diffusion coefficients aid in the design of devices which will have prescribed electrical parameters. This aspect has been amply described in an article by Tannenbaum<sup>2</sup>. Device parameters like base width, base resistance, emitter efficiency etc. depend on diffusion conditions and these can be predicted closely well if the concentration, nature of distribution, and diffusion constants of the impurities are known beforehand.

So in either way, knowledge of the diffusion profile and the related diffusion constants of the impurities is essential and in this work an attempt is made to evaluate



the profile of phosphorous distribution in p type silicon under different temperature conditions. Some of the anomalies, which have been reported in the literature, in case of diffusion under some specific conditions, are of main concern in this work.

## CHAPTER - 2

LAWS OF DIFFUSION

There are two laws governing the process of diffusion in solids.

$$\text{First Law : } J = - D \frac{\partial C}{\partial X}$$

$$\text{Second Law : } \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}$$

The First Law governs the flux  $J$  and concentration gradient  $\partial C / \partial X$  where as the second one is concerned with the spatial distribution of impurities with respect to time. These two laws put together are called Fick's laws.

The law of interest to semiconductor technologist is the second one as the solution of this law for the given diffusion conditions ie time, temperature and concentration describes the impurity distribution in the solid. Solution of this equations comes out to be different depending upon the boundary conditions and a look at ordinary diffusion conditions will be helpful in arriving at these boundary conditions.

In most of the cases what we have is a diffusion furnace whose central zone temperature can be kept constant

within  $\pm 1^\circ\text{C}$ , inside which one can keep a quartz tube to house the wafers. The dopant mixed with the carrier gas will be let in constantly into the quartz tube, the amount of gases being recorded by individual flow meters. If a liquid source like phosphorous-oxy chloride is being used oxygen also has to be used along with the carrier so as to facilitate the dissociation of phosphorous-oxy chloride into  $\text{P}_2\text{O}_5$  to form a local source near the wafer and also to protect the silicon surface. Through out the diffusion the same rate of flow gases is maintained through the furnace. This arrangement ensures a constant supply of the dopant near the surface and this becomes an important boundary condition in the solution of Fick's second law. Because no impurities of the same conductivity type are present in the wafer at the start of diffusion, we can see that at  $t=0$ ,  $C=0$ .

Under these conditions solution of second law can be seen to be<sup>3</sup>

$$C(x, t) = C_s \operatorname{erfc} x/2\sqrt{Dt} \quad \dots\dots\dots(1)$$

where  $C(x, t)$  is the concentration of the diffused impurity at a distance  $x$  from the surface after a time  $t$ .  $C_s$  represents the surface concentration;  $D$  and  $t$  represent the diffusion constant and time of diffusion respectively.

Though this error function solution describes satisfactorily

the infinite source diffusion in some cases, there are some cases where the distribution does not follow exactly this solution. It has been found that a moving boundary concept has to be introduced alongwith two diffusion constants into the boundary conditions to arrive at the diffusion profile under these special cases. These special conditions and how a moving boundary concept has taken shape are the subjects of the next chapter. However the solutions of the diffusion equation under these conditions are mentioned below.

In this approach it is assumed that there are two species of phosphorous diffusing into silicon preceeded by a region where there is no change in the concentration of impurities. A model fitting these assumptions is shown in Figure 1.

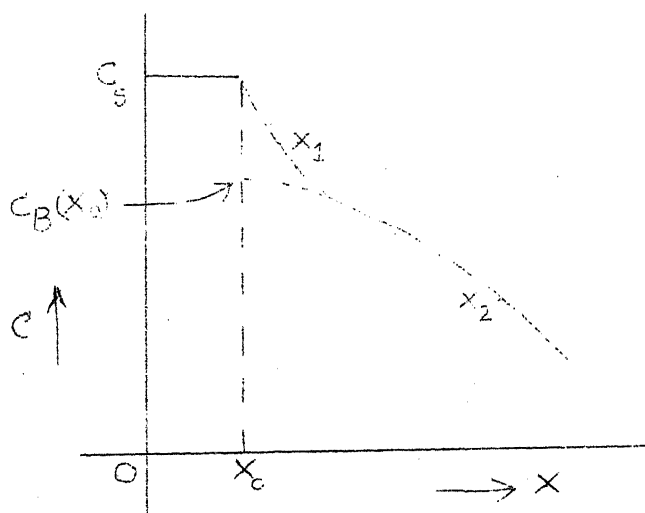


FIGURE - 1

It consists of three distinct regions, a constant surface concentration region followed by a transition region and then the normal diffusion region. The assumed moving boundary is shown to be lying at a distance  $x_0$  from the surface and for getting solutions of the diffusion equations it will be assumed that the position of the phase boundary is directly proportional to the time the surface is exposed to diffusion, ie  $x_0 = \alpha t$ . This boundary condition can be easily verified in practice and the validity of this is discussed by Tsai<sup>4</sup>. The transition region consists of the two types of diffusing species A and B where as the normal diffusion region consists of only one species B. It is also assumed that for a given temperature the concentration of the fast diffusing species B is constant at the phase boundary and the ratio  $C_B(x_0)/C_s$  is defined as  $K$ . Under these conditions one can write down the two diffusion equations for the two species. They are,

$$\partial C_A / \partial t = D_A (\partial^2 C_A / \partial x^2)$$

$$\text{and } \partial C_B / \partial t = D_B (\partial^2 C_B / \partial x^2)$$

where  $D_A$  and  $D_B$  are the diffusion constants of the two species A and B.  $C_A$  and  $C_B$  are the concentration of the species at distance  $x$  from the surface.

Boundary conditions can be noted to be,

$$C_A(x, 0) = 0$$

$$C_B(x, 0) = 0$$

$$C_A(\infty, t) = 0$$

$$C_B(\infty, t) = 0$$

$$C_B(x_0) = K.C_s \text{ and } C_A(x_0) = (1-K)C_s$$

Solutions to the two diffusion equations with the above mentioned boundary conditions are<sup>4</sup>:

$$C_A(x, t) = \frac{(1-K)}{2} C_s \exp \left[ \frac{-\alpha}{2D_A} (x - \alpha t) \right] \left[ \operatorname{erfc} \frac{x + \alpha t}{2\sqrt{D_A t}} + \operatorname{erfc} \frac{x - 3\alpha t}{2\sqrt{D_A t}} \right]$$

and

$$C_B(x, t) = \frac{K}{2} C_s \exp \left[ \frac{-\alpha}{2D_B} (x - \alpha t) \right] \left[ \operatorname{erfc} \frac{x + \alpha t}{2\sqrt{D_B t}} + \operatorname{erfc} \frac{x - 3\alpha t}{2\sqrt{D_B t}} \right]$$

for a total solution

$$\text{for } x < x_0, \quad C = C_s$$

$$\text{and } x > x_0 \quad C = C_A(x, t) + C_B(x, t).$$

This is the solution of Fick's law under the above mentioned conditions.

## CHAPTER - 3

DEEP AND SHALLOW DIFFUSIONS

The laws of diffusion and how far do they describe the practical diffusion profiles forms an important aspect of diffusion study, as has already been indicated.

In the history of diffusion in semiconductors, first attempts were made by Fuller, Dunlap and others to get p-n junctions and they have reported the diffusion constants of some impurities of interest in Germanium around 1952<sup>5,6,7</sup>.

Dunlap diffused antimony in germanium and evaluated the diffusion constants by two methods, one being radio active tracer method and the other p-n junction method using a thermal probe to detect the junction.

In the same year Fuller from Bell Telephone Laboratories reported his results of diffusion of As, Sb, In and Zn in Germanium following a different method. Diffusion into two specimens of two different resistivities  $\rho_1$  and  $\rho_2$  was done for the same time under identical conditions.

If the experiment is started with p type specimens having gallium previously distributed through out uniformly, and  $\sigma_1$  and  $\sigma_2$  are the conductivities of the two

specimens respectively, then,

$$\sigma_1 = e p_1 u \quad \text{and} \quad \sigma_2 = e p_2 u$$

$$\text{from this } p_1 = \frac{\sigma_1}{e u} \quad \text{and} \quad p_2 = \frac{\sigma_2}{e u}$$

Assuming complete ionisation,

$$C_{A1} = \frac{\sigma_1}{e u} \quad \text{and} \quad C_{A2} = \frac{\sigma_2}{e u}$$

Diffusion into these specimens was done and the depths  $x_1$  and  $x_2$  upto which the impurity penetrates were found. Assuming that the diffusion has followed error function solution, one must have

$$C(x_1, t) = C_0 \operatorname{erfc} \frac{x_1}{2\sqrt{Dt}} \quad \text{and} \quad C(x_2, t) = C_0 \operatorname{erfc} \frac{x_2}{2\sqrt{Dt}}$$

But by the definition of junction these donor concentrations must be precisely same as the acceptor concentrations existing there.

$$\therefore \frac{\sigma_1}{e u} = C_0 \operatorname{erfc} \frac{x_1}{2\sqrt{Dt}} \quad \text{and} \quad \frac{\sigma_2}{e u} = C_0 \operatorname{erfc} \frac{x_2}{2\sqrt{Dt}}$$

$$\text{Dividing, } \frac{\operatorname{erfc} \frac{x_1}{2\sqrt{Dt}}}{\operatorname{erfc} \frac{x_2}{2\sqrt{Dt}}} = \frac{\sigma_1}{\sigma_2}$$



In this equation, the only unknown  $D$  can be evaluated. These calculations are based on the assumption that Fick's law was obeyed during diffusion. Attempts made to check this validity experimentally are given below.

This law requires that when times required to reach a fixed arbitrary concentration at successive distances are measured, the distances must be proportional to the square root of the time.

In the course of previous diffusions, it is evident that irrespective of the depth of location of p-n junction, the concentration of impurities near this layer will be always the same. The only thing that is happening is that with prolonged heating this layer is going deeper and deeper into the substrate. This shift of the diffusion profile with time is well represented by Dunlap.

It is possible to find this layer at a distance  $x_{j1}$  if the diffusion is allowed for a time  $t_1$  and at a different depth  $x_{j2}$ , for a time  $t_2$ . What all the above law requires

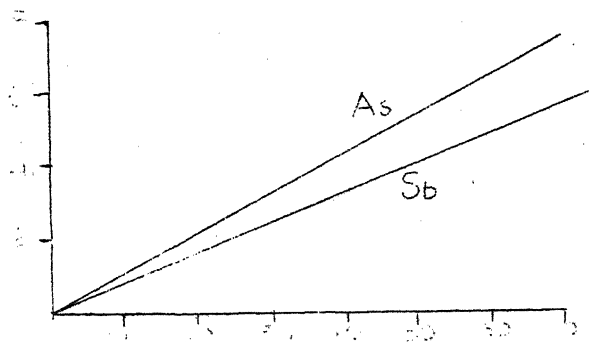


Figure 2

is that  $x_{j1} \propto t_1$  and  $x_{j2} \propto t_2$  or if we draw a graph between  $x$  and  $t$ , it must be a straight line<sup>8</sup>.

This is seen to be so from Figure 2. So it is evident that diffusion law is followed closely and that one can characterise the diffusion under these boundary conditions by the solution obtained from Fick's law.

Similar attempts were made later by Fuller and others<sup>7</sup>, to find out the diffusion constants of different impurity elements in silicon. The assumption that the concentration of the impurity near the surface remains constant has also been checked up.

In all these investigations and also in further investigations by various authors it was established that constant source diffusion can be described by erfc distribution. Experimental results of impurity concentration versus distance have been fitted into error function curves and the results were also satisfactory.

#### Exposure of Anamolies:

If one looks back into the graph for the verification of Fick's law the diffusion times encountered were hundreds of minutes and the diffusion depths also were correspondingly high. But with the advent of Integrated

Circuit Technology, short diffusion times and so correspondingly small diffusion depths have become common. Now-a-days shallow phosphorous diffusion is normally employed for the emitter of an n-p-n transistor. A typical value of the depth of this emitter diffusion will be around one micron<sup>9</sup>.

Following the work of Fuller and Ditzenberger, Tannenbaum continued the investigation of diffusion of phosphorous in silicon and reported that for relatively short diffusion times, the diffusion profile deviates considerably from the simple error function solution. It was found that electrically active phosphorous concentration remains constant for a few thousand angstroms from the surface<sup>10</sup>.

At the same time, a real check on the validity of error function distribution during constant source diffusion was made by Subashiev and others at the Academy of Sciences USSR<sup>11</sup>.

In this article they have suggested the existence of two diffusion constants instead of one and they have conclusively proved that for short diffusion ~~times~~ the impurity profile can not be described by error function solution.

In the present investigation, an attempt to check theoretical formulation for the experimentally observed

distribution of shallow phosphorous diffusion and the moving boundary concept is made at different temperatures. Practical diffusion profiles were obtained. Diffusion constants at different temperatures were evaluated from these curves and on the basis of the solutions given in cahpter 2, the concentration of impurities with respect to depth was recalculated. This calculated concentration is plotted back again on the same sheet, to compare it with the thecritical profile.

## CHAPTER - 4

EXPERIMENTAL WORKDoping System:

The doping system was set up in the top most shelf of the teakwood almirah specially got made for this purpose. A plan of flow of gases and the other accessories is given in Figures 3.

Presently three flow meters are being used two for nitrogen and one for oxygen. One of the two flow meters for nitrogen, the larger capacity one, is used for measuring the flow of nitrogen used as a carrier gas and this can be maintained at any required flow rate having a maximum value of 1450 cc/min, for sapphire ball. The stainless steel ball can extend the range of the flow meter above this, but in normal diffusion runs, 1450 cc/min of carrier gas is quite sufficient.

The other flow meter for nitrogen of smaller capacity, which is connected to the solenoid valve is meant for bubbling through the liquid dopant, which is  $\text{POCl}_3$  in this case. There are two possible states for the solenoid valve, normally closed (NC) and normally open (NO). When there is no power input to the valve NO side will be kept open for the gases. When power is on, functions of these gates

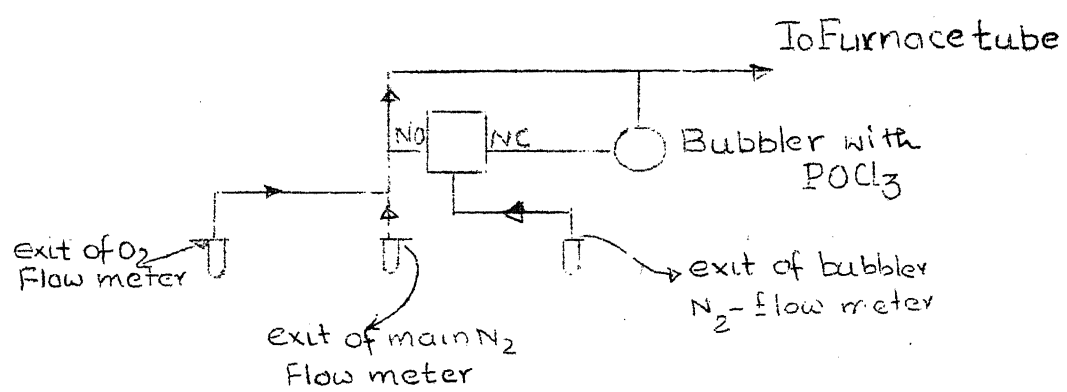


Figure-3

are just reversed. NC turns open and NO becomes shut.

Flow of oxygen is necessary during diffusion both for helping the dissociation of  $\text{POCl}_3$  into  $\text{P}_2\text{O}_5$ , so as to form a local source near silicon surface, from which actual phosphorous diffusion takes place and also for protecting the silicon surface.

Liquid dopant is kept in the bubbler shown in the diagram. When diffusion is to take place, the solenoid valve is kept on so that the side of the solenoid valve connected to the bubbler is open. Automatically, the other side of the valve which is connected to the main gas stream will be kept shut, so that no additional nitrogen can pass through the bubbler. This nitrogen which is bubbled through the dopant takes along with it the dopant and gets mixed with the main nitrogen and oxygen flows near the entrance of the furnace tube.

Temperature of the furnace is brought to the required value by setting the controller properly and it is advisable to measure the actual temperature inside the furnace with a platinum + platinum, 10% Rhodium thermo couple. It is observed that there is not much variation in the set temperature with moderate changes of carrier gas flow.

When the furnace is brought to the required temperature the two nitrogen flow meters are adjusted to the required flow rates. Solenoid valve is kept off during this time. Cleaned wafers are then loaded carefully into the wafer-carrier and it is pushed approximately to the centre of the furnace tube. Now the oxygen supply is turned on alongwith the solenoid valve. This is the time at which diffusion starts.

After allowing the nitrogen to pass through the bubbler for the required time of diffusion, solenoid valve is put off, thus cutting out the supply of dopant. Oxygen flow can be continued for a couple of minutes more to grow a thin oxide layer over the diffused surface which will offer protection from the surroundings. Then both main nitrogen and oxygen flows can be cut off and the wafer unloaded. This can be stored either in methanol or in a clean, covered petri-dish until further investigation is started.

#### Cleaning Procedures Prior to Diffusion

##### For Glass-ware:

All the beakers, petri-dishes etc are first washed with tap water thoroughly and then kept in hot KOH solution for about five minutes. After this they are taken out and washed in tap water and then kept in chromic acid



solution for about five minutes. Then they are taken out, washed in tap water, DI water and finally stored in a decontaminator unit for further use.

#### Cleaning of silicon wafers:

The 1 ohm-cm p type wafers used in this investigation were chemically polished and mirror finished, so that they can be directly effected to any one of the following cleaning procedures.

##### 1st Method:

Wafers are first cleaned ultrasonically in trichloroethylene for about five minutes.

Heating of these wafers is done successively in trichloroethylene and in a solution of equal parts, by volume, of  $H_2O_2$ ,  $NH_4OH$  and DI water for 30 minutes.

These are then taken out, rinsed in DI water and immersed in aquaregia for one minute.

After washing them in DI water, wafers are immersed in HF for 30 seconds. This is followed by a rinse in DI water. The two operations indicated in the above paragraph and this are repeated five times before a final through wash is given in DI water. These wafers are then stored in methanol.

Second Method:

Wafers are first cleaned ultrasonically in trichloroethylene, heated for five minutes in it and then washed thoroughly with DI water.

A solution of DI water, Hydrogen peroxide and  $\text{NH}_4\text{OH}$  in the ratio of 7:2:1, by volume, is prepared and heated to a temperature of  $80^\circ\text{C}$ . Wafers are then put into this hot solution for ten to fifteen minutes. After this, they are transferred into another beaker and washed thoroughly in DI water.

Another solution consisting of DI water,  $\text{H}_2\text{O}_2$  and  $\text{HCl}$  (35%) is prepared in the same ratio of 7:2:1, by volume. Wafers are put into this solution, when it is heated to a temperature of  $80^\circ\text{C}$ . After keeping them for ten to fifteen minutes, they are taken out, washed thoroughly in DI water and stored in methanol.

Of the two procedures the second one was found to be less time consuming and most of the time, this was followed.

Evaluation Procedure:

Various methods have been employed to get the concentration of impurities as a function of diffusion depth from into the silicon wafer, /the surface. In any method, it is

necessary to remove thin layers and observe the electrical or other physical parameters after each removal of layer and then relate these observed characteristics to the concentration of impurities there. When the diffusions were deep, this removal of layers was done by lapping with carefully designed jigs<sup>12</sup>.

Chemical etching can also be used for removing thin layers but here the problem is to control the thickness of layer removed each time.

Anodic oxidation followed by dissolving the  $\text{SiO}_2$  layer in HF offers a very precise control of the thickness of the layers removed with very good repeatability. Specially for shallow diffusions this is much more attractive because one can remove very thin layers of the order of  $100 \text{ \AA}$ . By varying the voltage applied to the anodic cell, thickness of the layer removed, can be varied. As in this investigation shallow diffusions are taken up this method of removal is employed and is found to be most convenient and time saving.

For this purpose, a special equipment was designed and is shown in figure 4, diagrammatically. It consists of stainless steel piece with a provision to connect to the vacuum pump on one side and on the other side

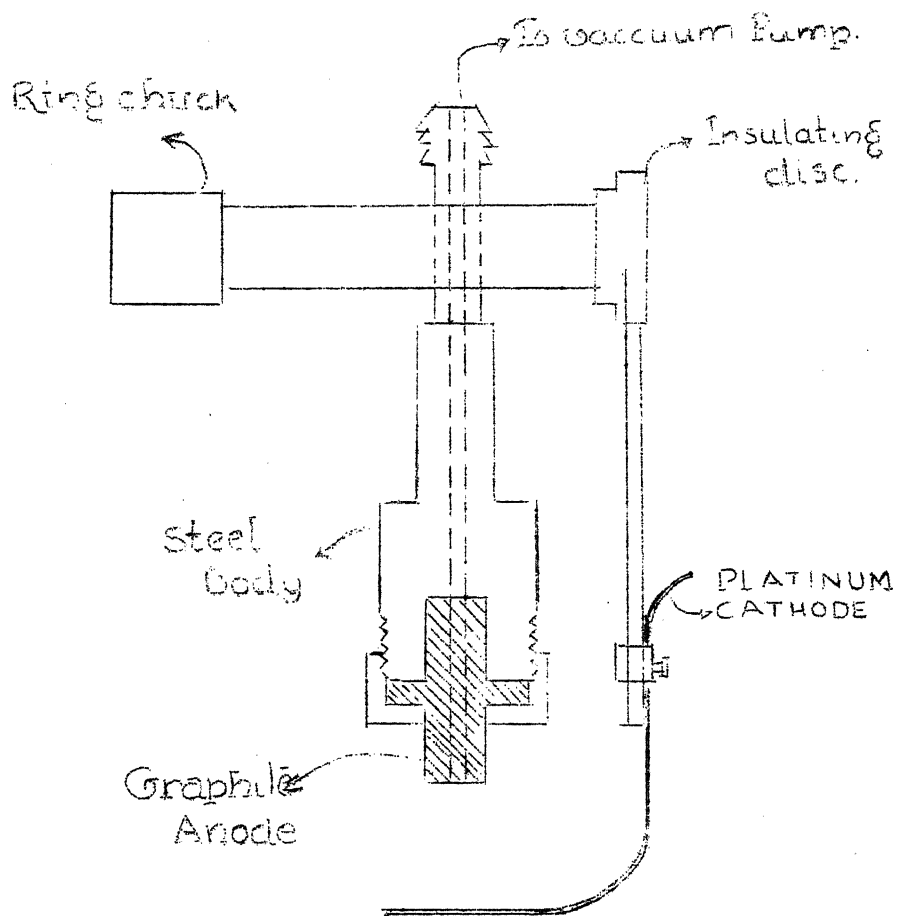


Figure-4  
Anodisation Equipment

a graphite piece can be fitted into this with the screw shown. Silicon piece can be held tight to this graphite piece. Stainless steel bar is connected to the positive of a DC supply so that in the process of anodisation the silicon piece becomes positive and acts as the anode.

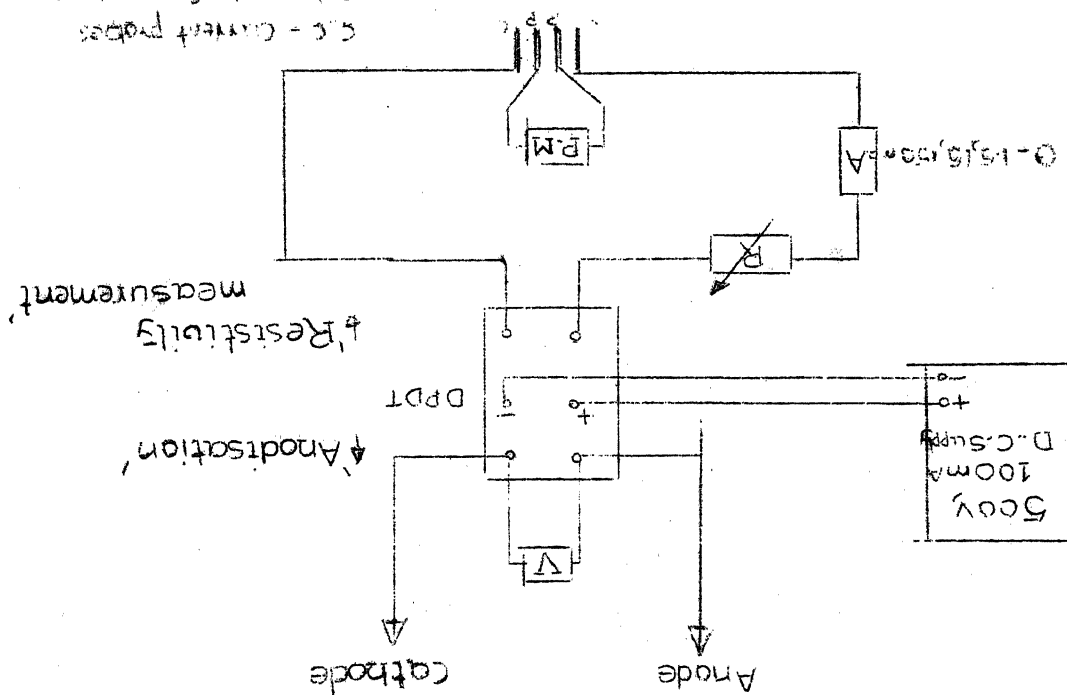
The cathode of the cell is made up of a platinum wire, wound in the form of a circular spring. Even though, at present this is giving almost uniform oxide layers, employment of a platinum foil would be more appropriate. This would help in establishing a more uniform ionic current density all along the wafer surface.

Both the anode and cathode are fitted into a horizontal bar (with appropriate isolation), permanently fixed in the ring of a travelling microscope. By loosening the screw of the vertical slider the anode-cathode assembly can be moved up and down and fixed at whatever height it is needed. An inherent advantage of this fixed anode-cathode arrangement is that, the height of the electrolytic column lying between them is same all along the experimentation and any variations in ionic current due to variation of electrolyte resistance, from one setting to another, are minimised.

A 0.04 normal solution of ethylene glycol and Potassium nitrate has been employed as the electrolytic solution<sup>13</sup>, with a small amount of water.

Electrolytic solution with the above composition is taken in a beaker and kept on the platform of the travelling microscope. Anode is connected to the positive of a 500V, 100mA power supply and the cathode is connected to the negative of it. Vacuum end of the stainless-steel piece is connected to a vacuum pump, through a trap. The silicon piece to be oxidised is held under the graphite piece by the vacuum pump. Electrical connections are shown in fi

There is a DPDT switch in the circuit one side of which is connected to the anode-cathode assembly and other side is connected to resistivity measurement circuit. Keeping the switch in anodisation position, voltage is set around 100V. For all the anodisations voltage between anode and cathode is maintained at  $100 \pm 2$  volts. After setting the power supply voltage to this value, the switch is thrown to the otherside so that there is no supply to anode and cathode. Now the anode-cathode assembly is lowered such that only the bottom surface of the silicon piece comes into contact with the electrolyte. When this is done the slider is moved just a little bit up so that the liquid forms a meniscus with the silicon piece. This will lessen the possibility of any liquid creeping to the other side of silicon piece and thus gradually establish a direct connection between the electrolyte and the graphite piece.



Arrangement for Anodisation

And

Sheet Resistance Measurement.

Figure 5A

This aspect of adjustment must be given sufficient importance because once direct conduction starts between electrolyte and graphite, the current through the circuit will not decrease with time as expected, and silicon dioxide layer ceases to form on the silicon piece.

Once the silicon piece is adjusted as above, switch is thrown to anodisation side. Initial current through the electrolyte will be around 50mA, for the conditions in this arrangement, and this current gradually starts falling off due to the formation of silicon dioxide on the surface of the silicon piece and the corresponding increase in path-resistance. In these experiments anodisation is stopped when the current falls off to a small value like 5 mA.

Vacuum pump is put off and the silicon piece is removed from the graphite piece with the help of tweezers. One must be careful here, because, if a little bit of vacuum is still left in the lines and the silicon wafer is tried to be taken away forcibly, it may break into pieces. That is why it will be better to have a stand-by sample diffused under the same conditions as the first one and should any thing happen to the first sample, evaluation can be started on the second one, thus saving a lot of time needed for cleaning and diffusing a fresh piece again.



The anodised piece, after removing from the graphite piece is well washed in tap water and then dropped in concentrated HF (48%) for about 30 seconds and again washed in water. This dissolves the silicon dioxide layer formed on silicon due to anodisation and exposes a fresh layer of silicon on which 4-point probe resistivity measurements can be made.

Determination of the thickness of silicon layer removed:

A rough estimate of the thickness of the silicon dioxide layer formed can be got from the colour of the film. After washing the anodised piece in water, it is allowed to dry and the colour can be seen under vertical fluorescent light. For the conditions employed in these experiments ie, 100V, 50mA to 5mA, and for the particular anodising solution used, colour of the film is always observed to be Brownish. This colour is also mostly uniform indicating that, the film of  $\text{SiO}_2$  is uniform. By referring to the colour charts<sup>14</sup>, one can see that this corresponds to a film thickness of 500 Å. As it is known that for the formation of 100 Å thick  $\text{SiO}_2$  layer only 44 Å of silicon is made use of, this 500 Å thick  $\text{SiO}_2$  layer corresponds to 220 Å of actual silicon removed<sup>15</sup>.

This is only a rough estimate of the silicon layer removed and a more accurate method would be to find out by the weight difference. For this, the weight of the sample before any anodisation, is taken exact upto six decimal places using a microbalance. After a known number of oxidations are done, the weight is taken again. The difference in weight gives the weight of total silicon removed. As each anodisation is done under exactly the same conditions, this weight difference by the number of anodisations gives the weight of each silicon layer removed. As the area of the piece will be known, assuming the density of silicon to be  $2.3 \text{ gms/cm}^3$ , thickness of each silicon layer removed can be computed.

In the investigations a  $287 \text{ mils} \times 287 \text{ mils}$  square sample was used, so that, if  $\Delta x$  is the thickness of each layer removed.

$$(287)^2 (25.4)^2 (10^{-4})^2 \Delta x \times \text{No of anodisations} = \frac{\text{Weight difference}}{\text{Density of silicon}}$$

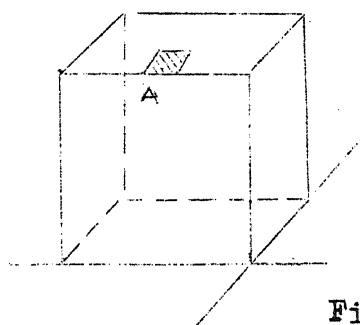
#### Sheet-Resistance measurements:-

After taking out the diffused sample from the furnace it is washed in HF for 30 seconds to remove the silicon dioxide formed on the top of it and first sheet resistance measurements are made on this surface.

For this, the DPDT switch is kept in Resistivity-measurement position in the circuit. As surface sheet resistance will be very less, of the order of a few ohms/sq, current in the order of 20-50 mA, through the current probes will be convenient to establish a potential difference accurately noticeable by the potentiometer, connected across the centre two voltage probes. The series resistance in the circuit and the voltage out put of the power supply are adjusted in such a way that the required current passes through the current probes. The potentiometer is standardised and the induced voltage between the two voltage probes is noted. Now the current is changed to some other value, by adjusting the power supply voltage and again the potential difference between the voltage probes is noted. The  $V/I$  ratio obtained with these two current levels must be approximately same or otherwise, readings at different current levels must be taken such that for two consecutive current levels the  $V/I$  ratio turns out to be approximately same.

Another point to be carefully noted in this context is the position of the sample under the probes. Variation in probe position on the sample from one set of readings to another set may make difference. To avoid this, the perspex cube on which the sample is being mounted is always kept exactly between two perpendicular guide lines

and then the silicon piece is adjusted on the top of this cube such that the same edge of the silicon piece is in contact with the front edge of the perspex cube, as shown in Fig.5 B



Figures 5B

Point A is marked on the perspex cube so that the lefthand side corner of the front edge of the silicon piece, is always set at this point. Finally the whole adjustment must be made in such away that the four probes of the header lie on straight line parallel to the edge and passing through centre of the top face of silicon piece.

The process of finding out the sheet resistance is followed by anodisation, washing and dissolving the  $\text{SiO}_2$  in HF and again sheet resistance measurements on the fresh layer exposed. This process must be continued until the p-n junction is reached, which can be detected by a hot probe.

#### Correction Factor:

Square samples having a side of 287 mils have been used for all the diffusions. Thickness of the piece

is found to be 9 mils. As diffusion takes place from both the faces correction factor corresponding to this situation are taken into account. This factor comes to be 4.5414 for the samples under consideration. Multiplication of  $V/I$  ratio at each stage gives the sheet resistance at that point.

Getting impurity concentration:

When sheet conductance and distance into the sample are plotted on a linear graph, the curve is found to be linear upto a point. This corresponds to a constant concentration region whose bulk conductivity is given by  $\partial\sigma_s/\partial x$ .

For getting the bulk conductivity at other points procedure suggested by<sup>16</sup> Evans and Donovan is followed.

According to that,

$$\rho(x) = \frac{0.4343 \rho_s(x)}{\frac{d}{dx} [\log_{10} \rho_s(x)]}$$

A curve has been fitted for each evaluation, between logarithm of sheet resistance and distance. The derivative of that at all the points is computed which gives the denominator of the above expression. As  $\rho_s(x)$  at each point is known, the complete expression can be calculated,

which gives the bulk resistivity at each and every point.

Reference to Irvin's<sup>17</sup> curve is then made to find the impurity concentration of phosphorous corresponding to this resistivity. All this procedure is illustrated by an example.

### Getting diffusion constants $D_A$ and $D_B$ :-

From the curve got by plotting concentration versus distance two points are taken one near the junction and the other one in the transition region. Near the junction, as we have only one diffusing species, faster type, this concentration corresponds to that species. As the time of diffusion and constant concentration region are known, the rate constant  $\alpha$  can be calculated. By extending the normal diffusion region curve backwards to the phase boundary  $C_B(x_0)$  can be found and thus  $K$ , which is  $C_B(x_0)/C_S$ . So in the equation,

$$C_B(x,t) = \frac{K}{2} C_S \exp \frac{-\alpha(x - \alpha t)}{2D_B} \operatorname{erfc} \frac{x + \alpha t}{2\sqrt{D_B t}} + \operatorname{erfc} \frac{x - \alpha t}{2\sqrt{D_B t}}$$

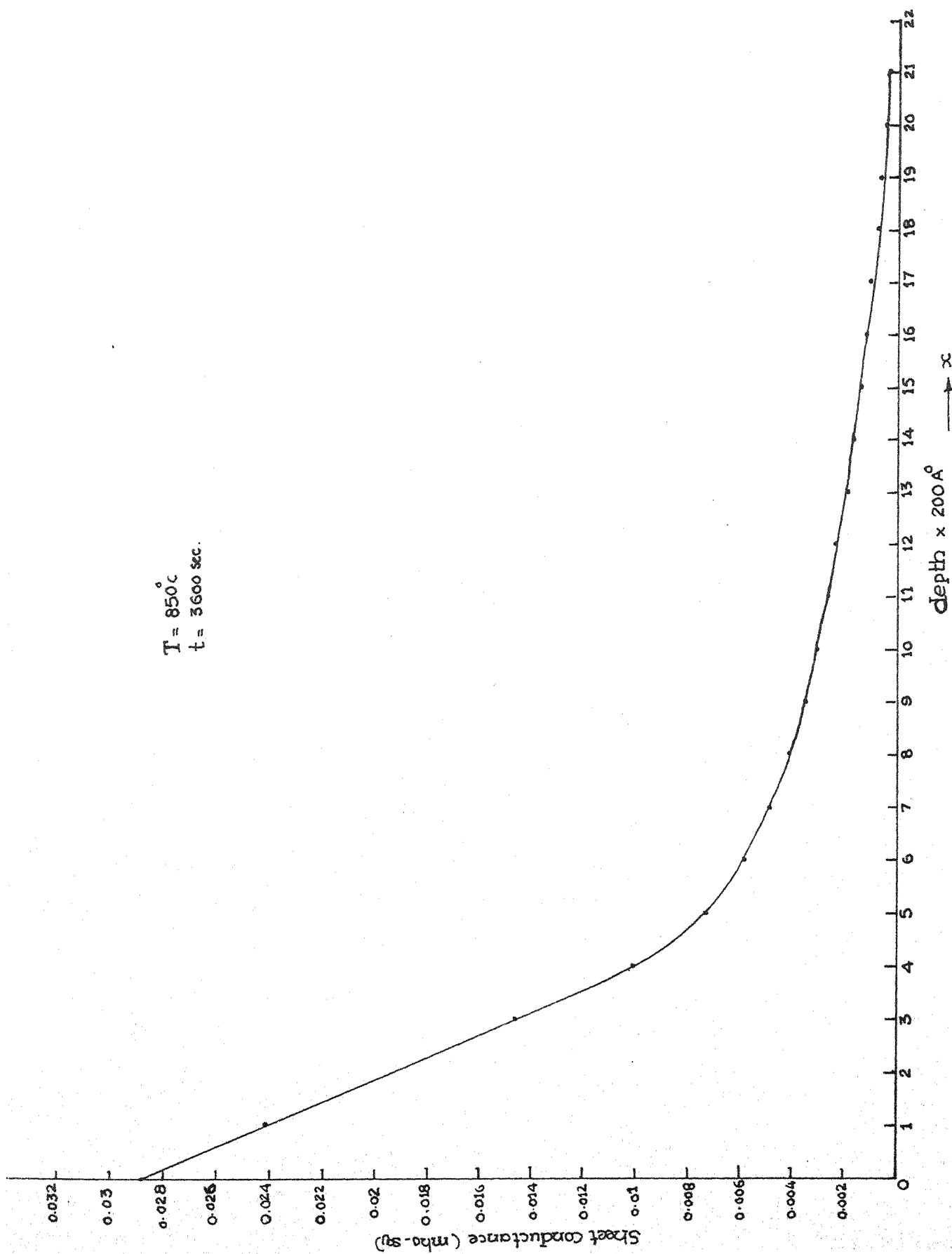
every thing except  $D_B$  is known and so  $D_B$  can be calculated. For this a computer program has been designed and is explained in the next chapter.

Similarly, for getting  $D_A$  the concentration of the impurity at a point in the transition region is noted. This will be the total concentration of the two species present there. To get the concentration of A species only, the concentration of B species is found from the backward extended curve and deducted from total concentration. Knowing  $C_A(x,t)$  as well as all other parameters,  $D_A$  is calculated.

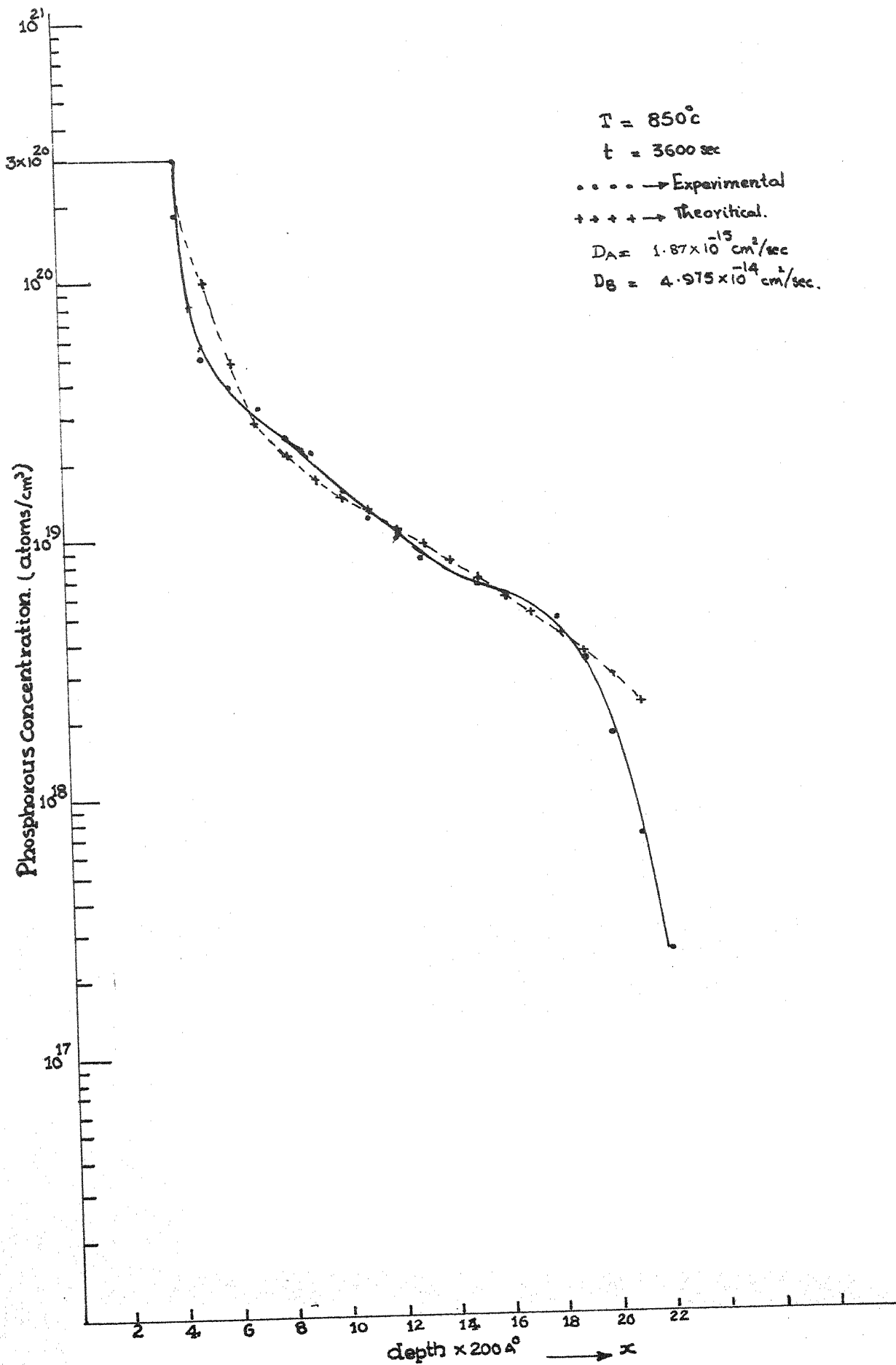
#### Checking up theory with experiment:

To verify whether the above mentioned solutions exactly describe the nature of distribution, the computed values of  $D_A$  and  $D_B$  are back substituted into their original equations and concentrations  $C_A(x,t)$  and  $C_B(x,t)$  are calculated at each point of interest. These two concentrations are added to give the total concentration of impurity at each point and this is plotted again on the same graph. One can see that there is good agreement between the two. Results are shown graphically from Figures 6 to 15.

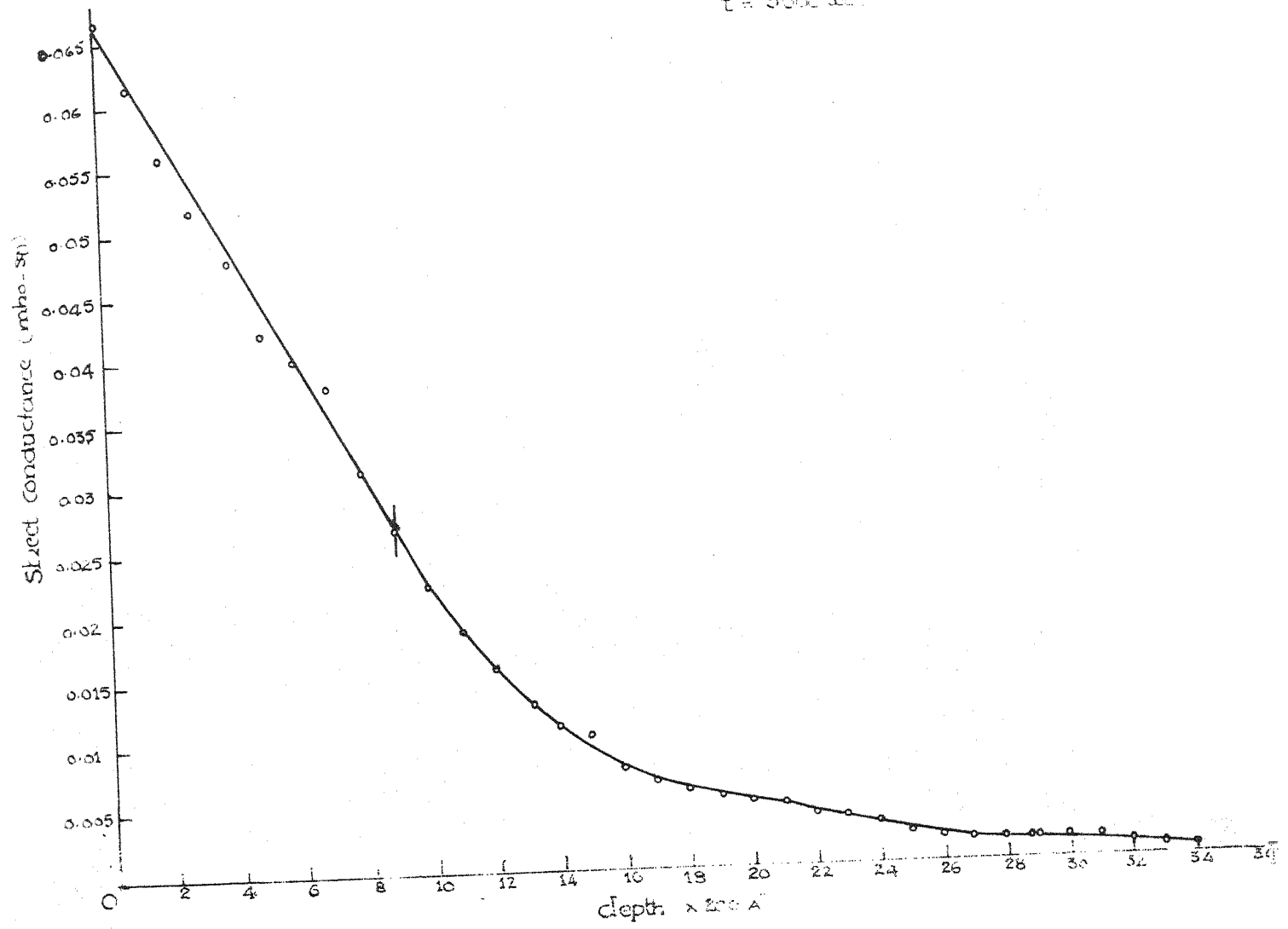
$T = 850^{\circ}\text{C}$   
 $t = 3600 \text{ sec.}$

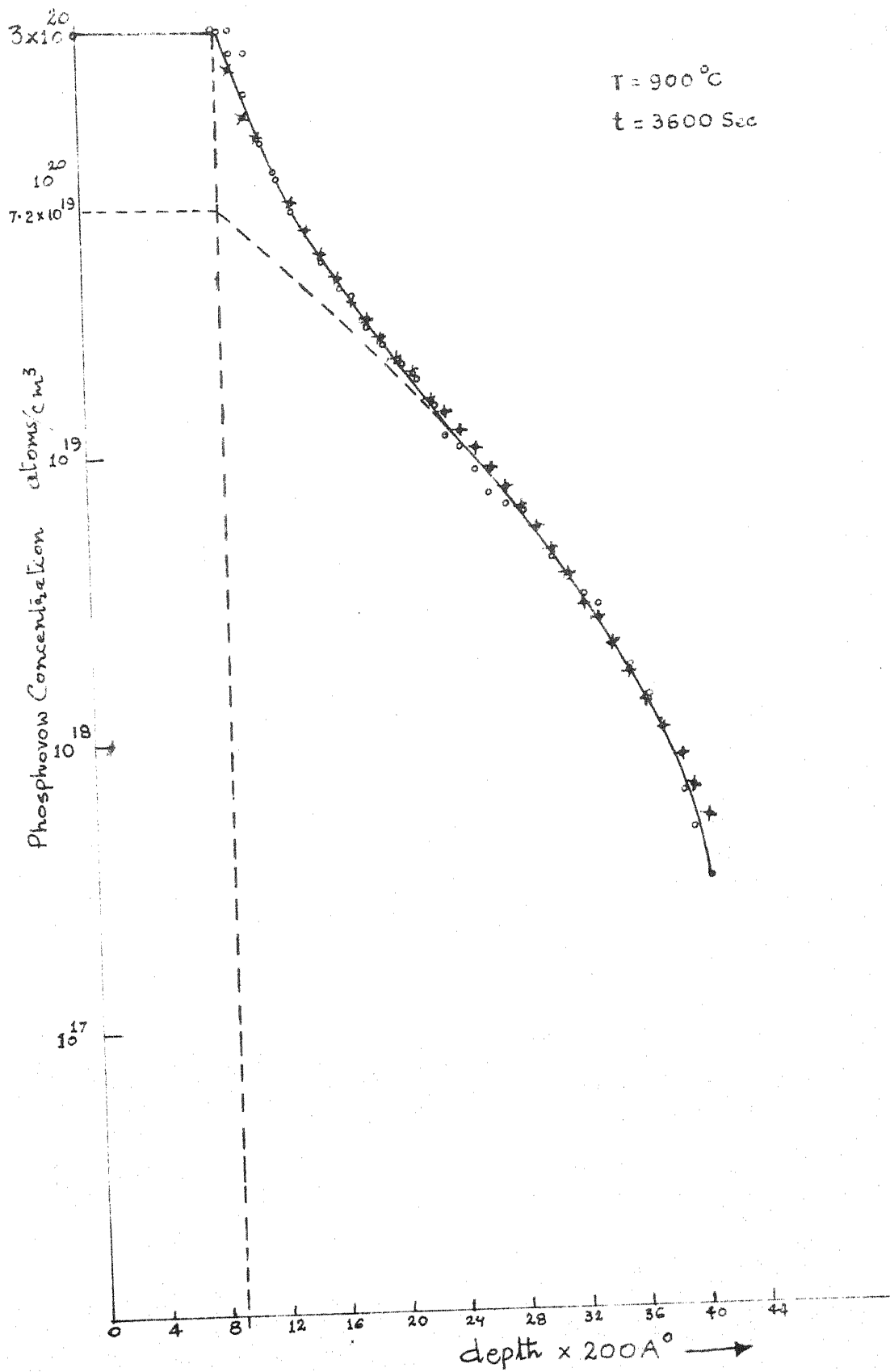


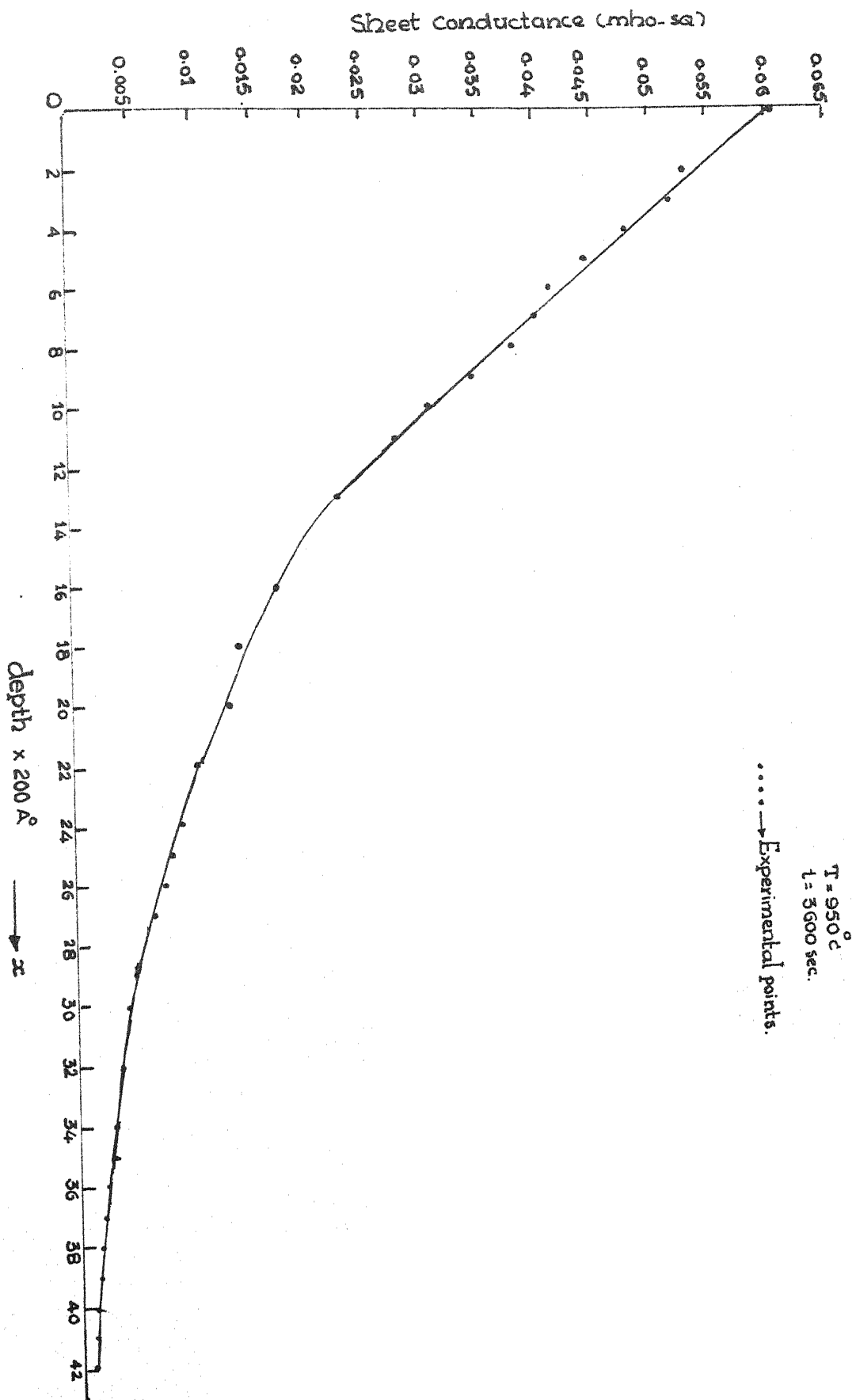


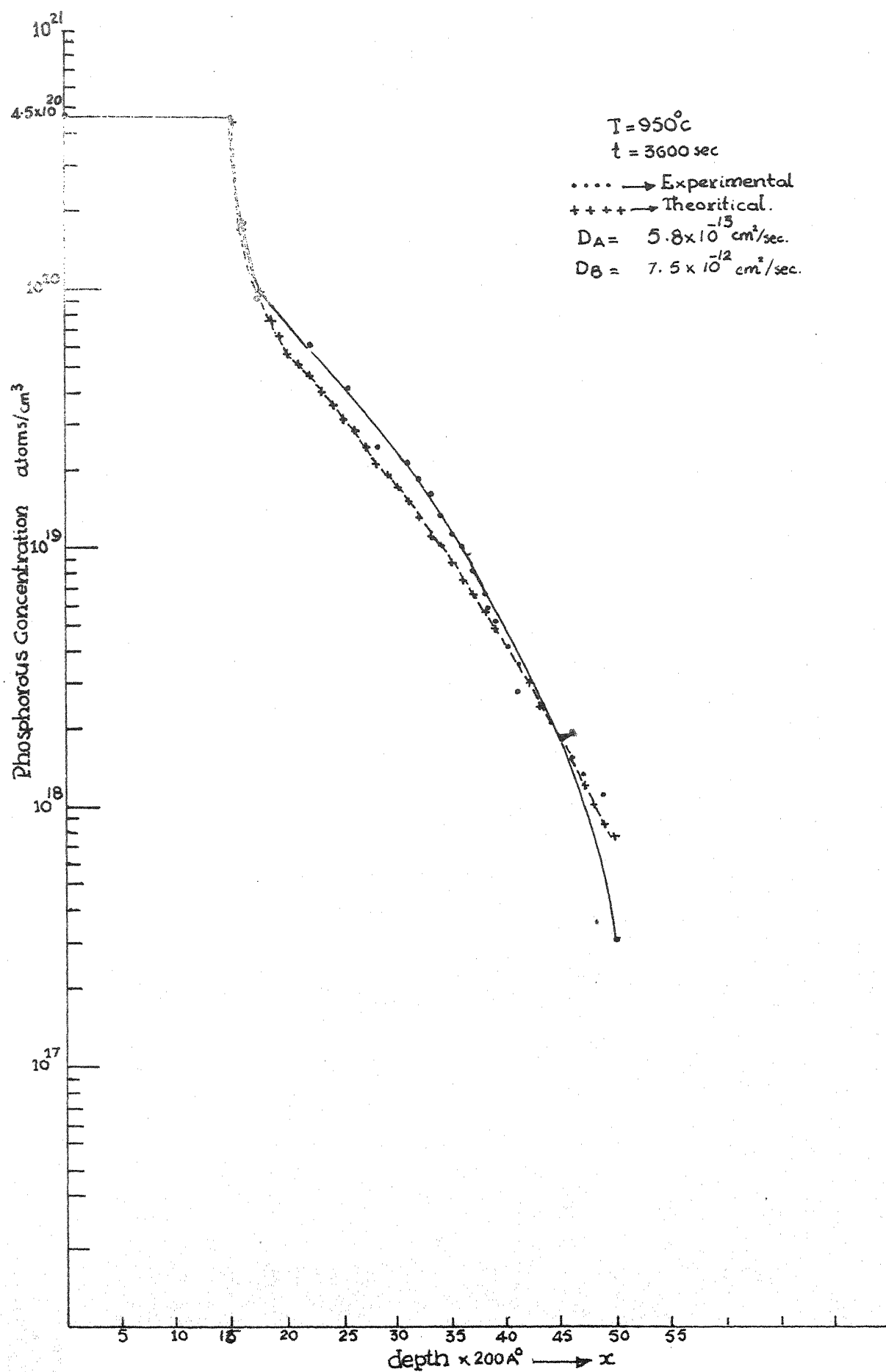


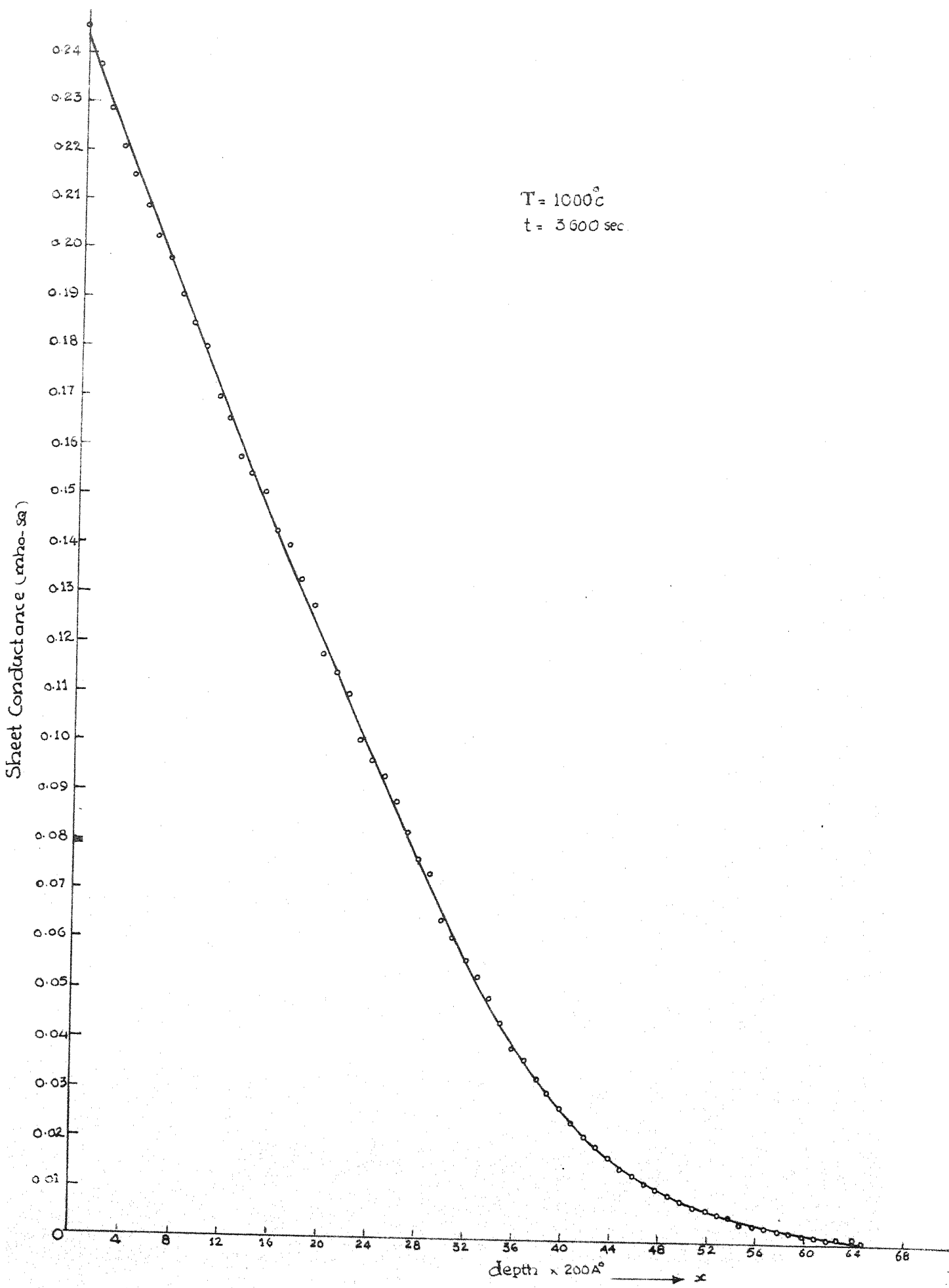
$T = 9000$   
 $t = 30000$

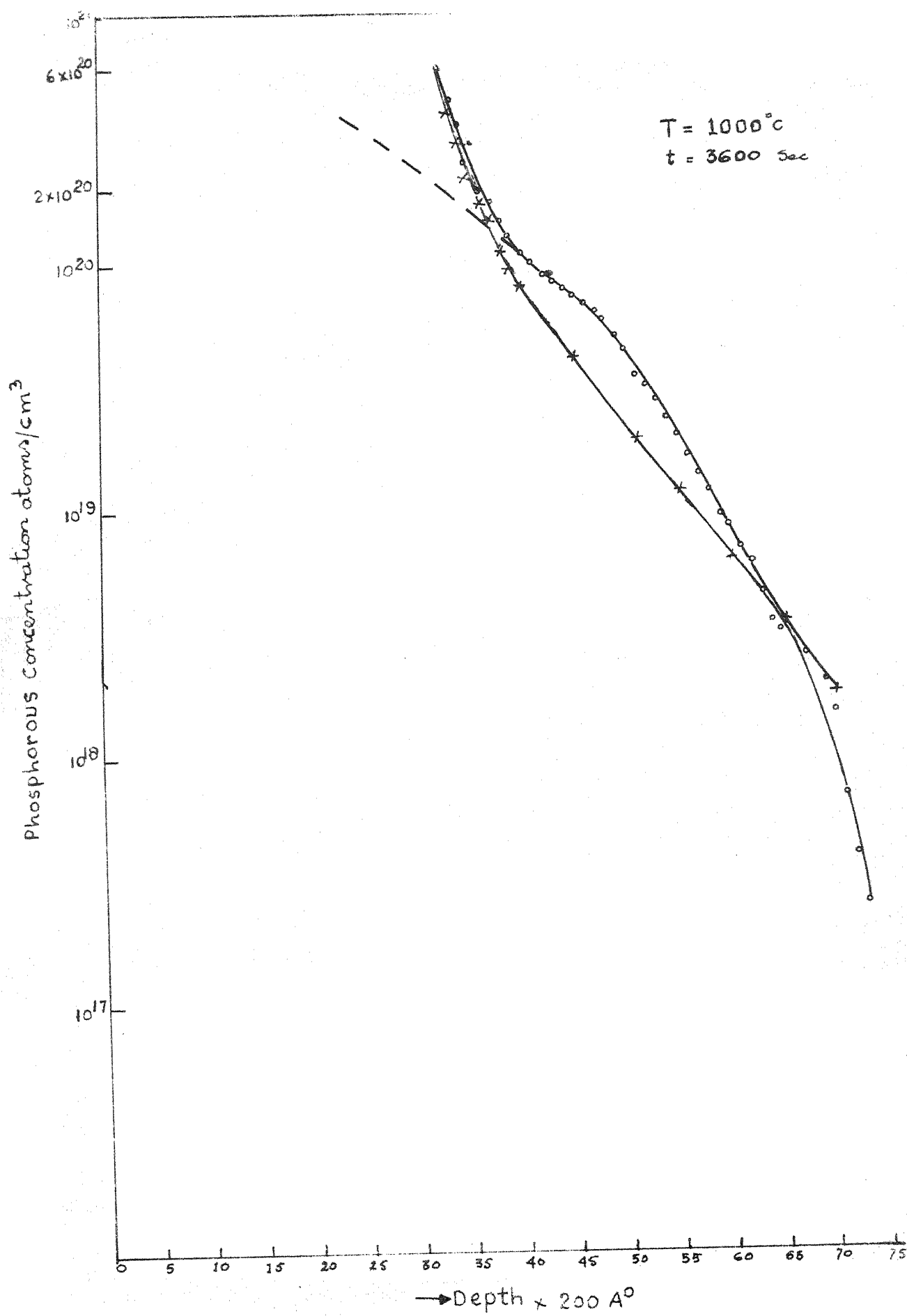


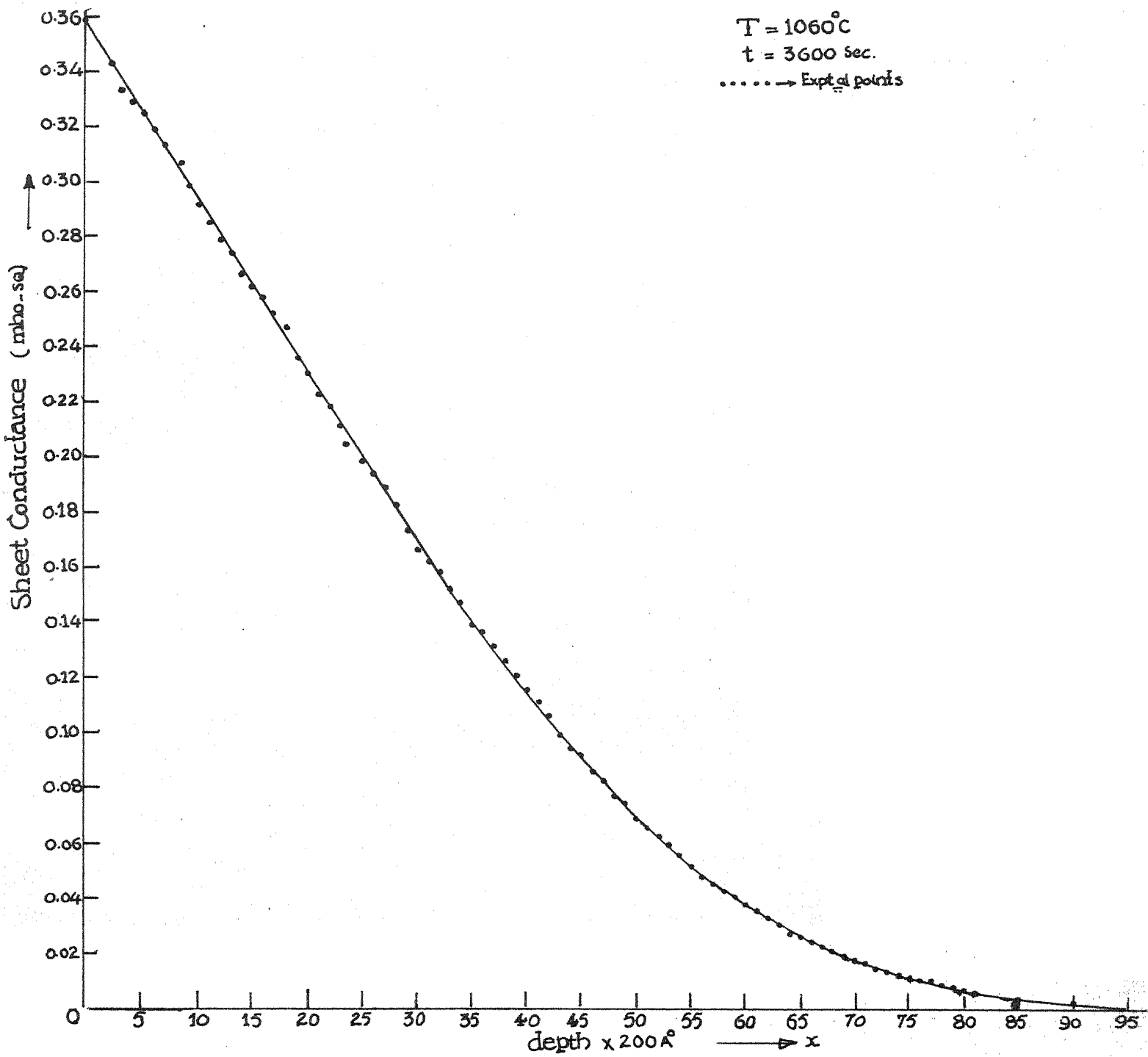




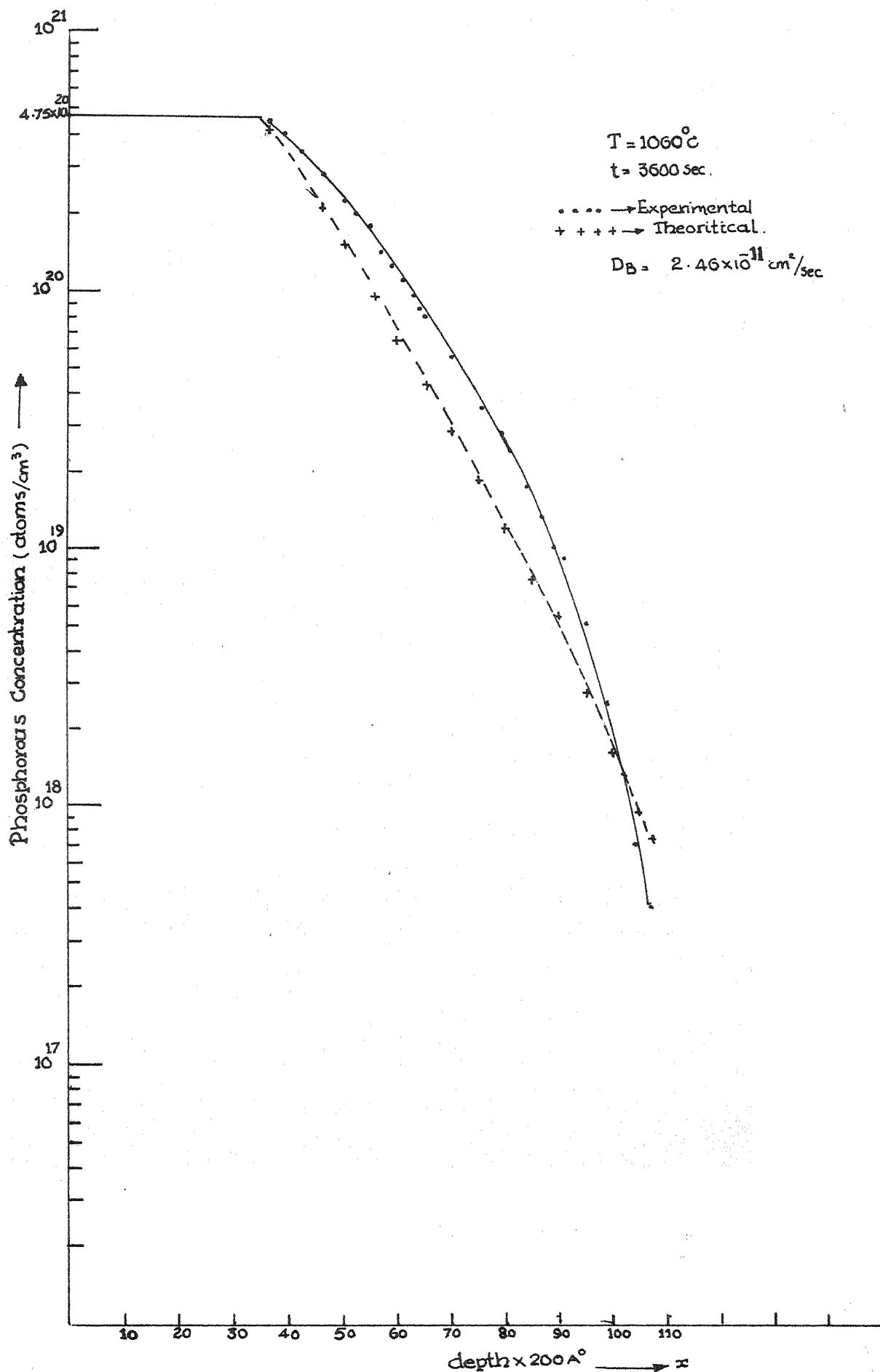












## CHAPTER - 5

MODEL EVALUATION

A typical evaluation example at 900°C is given below in detail.

Wafer started with : 1 ohm - cm p type

Dimensions of the Silicon piece 287 x 287 x 9 mils.

Diffusion temperature : 900°C

Diffusion time : 1 Hour.

Main nitrogen gas flow: 1450 cc/min

Nitrogen flow through the bubbler: 30 cc/min

Oxygen gas flow : 75 cc/min

Initial weight of the sample  
after diffusion and before any  
anodisation is done } 0.027865 gms

Anodising voltage =  $100 \pm 2$  V

Initial current through electrolyte =  $50 \pm 4$  mA

Final current when anodisation is stopped = 5mA.

Number of anodisations required)  
to reach p-n junction ) = 42

Weight after 25 number of anodisations = 0.027803 gms

Thickness of silicon layer removed each time =  $203 \frac{\text{Å}}{\text{Å}}$

As has already been mentioned, after each oxidation the sheet resistance was measured with Four point probe equipment. Sheet conductances corresponding to the first nine readings almost fall on a straight line, as shown in

the linear graph, and bulk conductivity of this surface layer is the slope of this straight line. This can be seen to be  $1/4.2 \times 10^{-4}$  approx, which corresponds to a concentration of  $3 \times 10^{20}/\text{cm}^3$  of phosphorous atoms. Bulk resistivity at all other points was found out using the expression already given. For calculating this, it is necessary to know the slope of logarithm of sheet resistance at each point, and so a curve is fitted between  $x$  and  $\rho_s$  with the help of computer and then the slope is computed. Those details are given below for  $900^\circ\text{C}$  diffusion.

The following polynomial was fitted to the values of  $x$  and  $\log(\rho_s)$

$$\text{Log}_{10}(\rho_s) = 0.828263 + 4.3744 x + 0.52744 x^2 - 8.9449x^3 + 8.957x^4$$

where  $x$  is in microns

This was differentiated at all the points to give the derivative and then  $\text{RHO}$  was calculated using the standard expression. Then from Irvin's curves concentration corresponding to each value of  $\text{RHO}$  was noted.

This concentration was plotted against  $x$  on a semi-log paper and is shown as the experimental curve.

X (microns)	$\rho_s$ (ohms/sq)	$\frac{d}{dx}(\log_{10} \rho_s)$	$\rho$ (ohms-cm)	G (atoms/cm <sup>3</sup> )
0.20	43.8	37987.2	$5 \times 10^{-4}$	$2.5 \times 10^{20}$
0.22	52.0	36892.9	$6.1 \times 10^{-4}$	$1.8 \times 10^{20}$
0.24	62.5	35773.2	$7.6 \times 10^{-4}$	$1.2 \times 10^{20}$
0.26	75.3	34645.2	$9.4 \times 10^{-4}$	$9 \times 10^{19}$
0.28	87.5	33526.0	$1.1 \times 10^{-3}$	$7 \times 10^{19}$
0.30	99.8	32433.0	$1.3 \times 10^{-3}$	$6 \times 10^{19}$
0.32	116.5	31383.2	$1.6 \times 10^{-3}$	$4.5 \times 10^{19}$
0.34	135.0	30394.0	$1.9 \times 10^{-3}$	$4 \times 10^{19}$
0.36	151.0	29482.5	$2.2 \times 10^{-3}$	$3.5 \times 10^{19}$
0.38	171.0	28665.8	$2.5 \times 10^{-3}$	$2.7 \times 10^{19}$
0.40	194.5	27961.3	$3 \times 10^{-3}$	$2.4 \times 10^{19}$
0.42	220.0	27386.0	$3.5 \times 10^{-3}$	$2 \times 10^{19}$
0.44	250.0	26957.3	$4.0 \times 10^{-3}$	$1.8 \times 10^{19}$
0.46	290.0	26692.2	$4.7 \times 10^{-3}$	$1.4 \times 10^{19}$
0.48	329.0	26608.0	$5.4 \times 10^{-3}$	$1.1 \times 10^{19}$
0.50	372.0	26721.9	$6.0 \times 10^{-3}$	$1.0 \times 10^{19}$
0.52	434.0	27051.1	$6.9 \times 10^{-3}$	$8.5 \times 10^{18}$
0.54	505.0	27612.8	$7.9 \times 10^{-3}$	$7 \times 10^{18}$
0.56	538.0	28424.2	$8.2 \times 10^{-3}$	$6.5 \times 10^{18}$
0.58	605.0	29502.5	$8.9 \times 10^{-3}$	$6 \times 10^{18}$
0.60	715.0	30864.8	$1.0 \times 10^{-2}$	$5.0 \times 10^{18}$
0.62	852.0	32528.4	$1.1 \times 10^{-2}$	$4.0 \times 10^{18}$
0.64	960.0	34510.5	$1.2 \times 10^{-2}$	$3.5 \times 10^{18}$

Contd. on the next page.

X (microns)	P <sub>s</sub> ohms/sq	$\frac{d}{dx}$ (log <sub>10</sub> P <sub>s</sub> )	$\rho$ (ohms-cm)	C (atoms/cm <sup>3</sup> )
0.66	1100.0	36828.3	1.3x10 <sup>-2</sup>	3x10 <sup>18</sup>
0.68	1300.0	39498.9	1.4x10 <sup>-2</sup>	2.8x10 <sup>18</sup>
0.70	1610.0	42539.7	1.6x10 <sup>-2</sup>	2.0x10 <sup>18</sup>
0.72	1950.0	45967.7	1.8x10 <sup>-2</sup>	1.7x10 <sup>18</sup>
0.74	2600.0	49800.1	2.2x10 <sup>-2</sup>	1.3x10 <sup>18</sup>
0.76	3010.0	54054.3	2.4x10 <sup>-2</sup>	1.0x10 <sup>18</sup>
0.78	4380.0	58747.3	3.2x10 <sup>-2</sup>	6.0x10 <sup>17</sup>
0.80	5430.0	63896.4	3.7x10 <sup>-2</sup>	4.5x10 <sup>17</sup>
0.82	7230.0	69518.7	4.5x10 <sup>-2</sup>	3x10 <sup>17</sup>

From the experimental curve two points were taken, one at  $x_1 = 0.24$  and another at  $x_2 = 0.70$  microns.

$$\text{Value of } K = \frac{C_B(x_0)}{C_s} = \frac{7.2 \times 10^{19}}{3.0 \times 10^{20}} = 0.24$$

The constant surface concentration region extends upto  $x_0 = 0.18 \times 10^{-4}$  cm.

$$\text{So, from } x_0 = \alpha t, \quad \alpha = \frac{0.18 \times 10^{-4}}{3600} = 5 \times 10^{-9}$$

At  $x_1$ ,  $C(x_1) = 1.2 \times 10^{20}$  and from the extended curve  $C_B(x_1) = 5 \times 10^{19}$ , so that  $C_A(x_1) = 7 \times 10^{19}$ .

This value of  $C_A(x_1)$  and the above given values of  $k, \alpha, t$

and  $x$  were substituted in the equation for  $C_A(x, t)$ , to get the value of the unknown term  $D_A$ .

Again, at  $x_2$ ,  $C_B(x_2) = 2 \times 10^{18}$ , and this value of concentration at  $x_2$  and all the above values of  $k$ ,  $\alpha$  and  $t$  were substituted into the equation for  $C_B(x, t)$ , to get the value of  $D_B$ .

The values of  $D_A$  and  $D_B$  calculated in the above manner are,

$$D_A = 1.27 \times 10^{-14}$$

and  $D_B = 6.2 \times 10^{-14}$

These values were substituted back into the two original equations and the concentrations  $C_A(x, t)$  and  $C_B(x, t)$  were calculated at all the points. The sum of these two gives the total concentration  $C(x, t)$ . These are tabulated for this case, as shown on the next page.

This concentration, calculated from the theoretical equations, was plotted again with respect to depth and is shown as the theoretical curve. As the experimental and theoretical curves are in good agreement, it can be concluded that the concept of two diffusion constants is valid. A discussion of the results is given in chapter 6 in a more detailed way.

$x$ (microns)	$C_A(x, t)$ atoms/cm <sup>3</sup>	$C_B(x, t)$ atoms/cm <sup>3</sup>	$C = C_A + C_B$ atoms/cm <sup>3</sup>
0.20	0.153832E 21	0.652550E 20	0.219087E 21
0.22	0.103781E 21	0.591042E 20	0.162885E 21
0.24	0.700000E 20	0.534811E 20	0.123481E 21
0.26	0.471956E 20	0.483291E 20	0.955247E 20
0.28	0.317975E 20	0.436005E 20	0.753981E 20
0.30	0.213974E 20	0.392552E 20	0.606527E 20
0.32	0.143711E 20	0.352595E 20	0.496306E 20
0.34	0.962369E 19	0.315848E 20	0.412085E 20
0.36	0.641692E 19	0.282073E 20	0.346242E 20
0.38	0.425309E 19	0.251066E 20	0.293597E 20
0.40	0.279631E 19	0.222650E 20	0.250613E 20
0.42	0.181952E 19	0.196671E 20	0.214866E 20
0.44	0.116872E 19	0.172988E 20	0.184675E 20
0.46	0.739074E 18	0.151474E 20	0.158864E 20
0.48	0.458906E 18	0.132005E 20	0.136594E 20
0.50	0.279048E 18	0.114465E 20	0.117256E 20
0.52	0.165757E 18	0.987388E 19	0.100396E 20
0.54	0.959627E 17	0.847110E 19	0.856707E 19
0.56	0.540328E 17	0.722674E 19	0.728077E 19
0.58	0.295338E 17	0.612933E 19	0.615886E 19
0.60	0.156446E 17	0.516742E 19	0.518306E 19
0.62	0.801962E 16	0.432964E 19	0.433766E 19
0.64	0.397313E 16	0.360478E 19	0.360875E 19
0.66	0.190027E 16	0.298188E 19	0.298378E 19
0.68	0.876567E 15	0.245034E 19	0.245121E 19
0.70	0.389650E 15	0.200000E 19	0.200039E 19
0.72	0.166790E 15	0.162125E 19	0.162141E 19
0.74	0.687059E 14	0.130507E 19	0.130514E 19
0.76	0.272215E 14	0.104313E 19	0.104315E 19
0.78	0.103684E 14	0.827782E 18	0.827792E 18
0.80	0.379506E 13	0.652123E 18	0.652127E 18
0.82	0.133435E 13	0.509965E 18	0.509966E 18

## CHAPTER - 6

DISCUSSION OF THE RESULTS

From the plots at different temperatures, it is evident that, the distribution of impurities can be characterised by three distinct regions. As has already been indicated, these are a constant concentration region, a transition region, followed by the normal diffusion region.

Presence of constant surface concentration region has been established by many authors. Tannenbaum was the first to give a detailed account of this for phosphorous diffusion in silicon. This was followed by many reports about the existence of a constant surface concentration during Boron diffusion as well as under different conditions of phosphorous diffusion.

There is always a difference between the concentrations of phosphorous atoms, as measured by electrical means, and the total phosphorous concentration as can be obtained by radio tracer measurements. How a flat region arises near the surface can be explained in the following way.

At high concentrations of phosphorous, diffusion introduces dislocation networks, reaching such densities



as  $5 \times 10^9 \text{ cm/cm}^3$  near the surface. Then networks can be found to be reaching such depths as  $1.5 \mu$  from the surface<sup>18</sup>. At still greater distances these networks degenerate into individual dislocations and finally reaching the densities present in the original sample, before diffusion. This generation of dislocation network was found to start with a concentration of  $10^{20}/\text{cm}^3$  of electrically active phosphorous atoms. These diffusion induced dislocations have predominant edge character and as already there is a supersaturation of phosphorous atoms they precipitate along the dislocations and at other strain centres. That this is so, has been experimentally verified by using electron microscopy<sup>19</sup>.

The fact that impurity concentration in the range of  $10^{20}/\text{cm}^3$  gives rise to dislocation formation can be seen in the following way.

Because of diffusion of impurities there is a mismatch between solute and solvent and the strain due to this mismatch will be removed by the formation of dislocations. If  $\sigma$  denotes the stress induced due to this impurity concentration, for shallow diffusions, it has been shown by Thai<sup>20</sup>, that this is related to the impurity concentration by the relation

$$\sigma = \frac{BEC}{1 - \nu} ,$$

where  $\beta$  = Solute lattice contraction coefficient

$E$  = Young's Modulus of silicon

$\nu$  = Poisson's ratio

and  $C$  = concentration of impurity

If this induced stress exceeds the flow stress of the material, given by  $bN^{\frac{1}{2}}\mu/w$ ,

where,  $b$  is the magnitude of Burgers vector

$N$  is the dislocation density

$\mu$  is the shear modulus

and  $w$  is a numerical factor ranging from 3 to 5

$N$ , in itself is related to the concentration of impurities by the simple relation  $N = Q\beta C$  where  $Q$  is a constant.  
So flow stress =  $b(Q\beta C)^{\frac{1}{2}}\mu / w$ .

Plastic flow occurs when induced stress exceeds this, i.e. when.

$$C \geq \frac{Q}{\beta} \cdot \left[ \frac{\mu b (1 - \nu)}{wE} \right]^2$$

Substituting the values of various terms in this expression, it can be seen that this concentration comes to be about  $5 \times 10^{19}/\text{cm}^3$ .

This value of concentration, where plastic flow begins i.e. dislocation networks begin to form, is in

where  $\beta$  = Solute lattice contraction coefficient

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and  $C$  = concentration of impurity

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Substituting the values of various terms in this expression, it can be seen that this concentration comes to be about  $5 \times 10^{19}/\text{cm}^3$ .

This value of concentration, where plastic flow begins i.e. dislocation networks begin to form, is in

confirmation with the concentration value where the electrical measurements deviate from radio tracer measurements. Once the concentration of impurities exceeds this, the silicon matrix into which these impurities are introduced starts adjusting itself by thermally-activated self diffusion. That is why the solute atoms will propagate to the dislocations and to other discrete strain centres and this results in precipitation. So during diffusion, the strained lattice attempts to maintain in solution an impurity content of not more than the solubility limit corresponding to the thermodynamic stability. This only can be measured by electrical methods and is equivalent to the total phosphorous in true solid solution.

Knowing the density of dislocations with respect to distance into the wafer, one can calculate the amount of precipitation at each and every point and by subtracting this precipitation profile from the ideal error function profile, the true curve for the electrically active phosphorous will be obtained. This phenomenon leads to a constant surface concentration.

In the present investigations also a constant surface concentration has been observed. When the measured sheet conductance is plotted against the distance, a curve

results in which the slope is constant upto a particular distance. That this is so, is evident from all the graphs shown, at different temperatures. As the slope of sheet conductance versus distance gives the bulk conductivity, after finding the slope, reference is made to Irvin's curve to get the surface concentration. When ever there is a small deviation of some points from the straight line, it is believed that it is due to the variation of probes position on the wafer from one reading to another. The general trend of the distribution is clearly linear near the surface, thus establishing the fact that surface concentration remains constant, upto a distance.

It was assumed, while getting the solutions for diffusion equations, that a phase boundary exists and the end of this constant surface concentration region corresponds to this.

Investigation by Schmidt et al<sup>21</sup> revealed that the precipitations are in the form of a compound of silicon and phosphorous and were verified to be silicon phosphide. Once the dislocation networks cease to exist at the phase boundary some of the precipitated material may take up substitutional places, thus contributing to another diffusion coefficient. If it is assumed that

molecular silicon phosphide migrates without dissociation, its diffusion constant will be lower than elemental phosphorous. This has also been verified in these investigations. For all the cases value of the constant  $D_A$  is smaller than  $D_B$ . Thus it is probable that in the region immediately following the phase boundary both the species are present and the total electrically active phosphorous concentration will be the sum of the two individual concentrations. As the normal diffusion region is reached, the concentration of A species falls off rapidly and this infact can be seen in the model evaluation given.

APPENDIX

Two computer program packages, 'BULKR' and 'DIFCOF' have been used to compute the bulk resistance and the diffusion coefficient (and related calculations) respectively. A brief outline of the methods adopted in them is given below.

'BULKR' accepts as input (with Runtime format facility) the number of observations of  $X$  made, the values of  $X$  and the corresponding values of  $\rho_s$ . The values of  $\log_{10} \rho_s$  are computed using the built in FORTRAN function  $\text{ALOGIO}(Z)$ .

The values of  $X$  and  $\log_{10} \rho_s$  are fed to a routine 'POLY'. This routine obtains a good polynomial fit for the sets of values given. Given a number  $n$ , the values of  $x$  and  $y$ , a routine 'CURVE' obtains an  $n^{\text{th}}$  degree polynomial for the  $Y$  in terms of  $x$ . The method employed is the Regression coefficient method. The Routine 'CURVE' computes the  $n + 1$  coefficients of the  $n^{\text{th}}$  degree polynomial; also it computes the values of  $Y$  at the given values of  $x$  using the polynomial and compares them with the given values of  $x$  and obtains the standard deviation. 'POLY' repeatedly calls 'CURVE' for various values of  $n$  and selects that polynomial which has minimum standard deviation. The limits of  $n$  between which all degrees are tried are controllable through appropriate input parameters.

'BULK' proceeds with the best polynomial obtained and computes the polynomial for the derivative of  $\log_{10} \rho_s$  by algebraic differentiation. Using this the values of the derivative of  $\log_{10} \rho_s$  are computed at various  $x$ . Then using the formula  $= 0.4343 \rho_s / \frac{d}{dx} (\log_{10} \rho_s)$  the bulk resistivity is computed. A typical input to and output of the package 'BULKR' are given below.

The input is as follows Format is 3 I 5 for the first card to give the number of observations the limits of the degrees of polynomials to be tried; 10E 8.2 for values of  $x$  and  $\rho_s$ .

```
19      3      6
.10E-4,.12E-4,.14E-4,.16E-4,.18E-4,.20E-4,.22E-4,.24E-4,.26E-4,
.28E-4,.30E-4,.32E-4,.34E-4,.36E-4,.40E-4,.42E-4,.44E-4,.46E-4,
.136E+3,.172E+3,.208E+3,.246E+3,.280E+3,.330E+3,.377E+3,.554E+4,
.627E+3,.815E+3,.957E+3,.131E+4,.272E+4,.754E+4,.122E+5,.192E+5.
```

The output is as follows:

THE FOLLOWING ARE VALUES OF  $\log_{10} \rho_{HS}$

```
.213354E + 1 .223553E + 1, .231806E+1,.239094E+1,.244716E+1,
.251851E + 1 .257634E + 1 .263649E + 1 .274351E + 1
.279727E + 1 .291116E + 1 .298091E + 1 .311661E + 1
.328217E + 1 .343457E + 1 .364345E + 1 .387737E + 1
.408458E + 1 .438217E + 1
```



POLYNOMIAL FIT BEGINS

DEGREE = 3 S = 0.023032

DEGREE = 4 S = 0.018464

DEGREE = 5 S = 0.014035

DEGREE = 6 S = 0.015431

THEREFORE SELECTED DEGREE IS = 5 FOR WHICH S = 0.014035

THE FOLLOWING ARE COEFFICIENTS OF POLYNOMIAL OF LOG RHOS

$X_0$	$X_1$	$X_2$	$X_3$
0.249768E + 1	-0.162668E + 2	0.205037E + 3	-0.9608E + 3
$X_4$	$X_5$		
0.208958E + 4	-0.154960E + 4		

THE FOLLOWING ARE COEFFICIENTS OF POLYNOMIAL OF DERIVATIVE  
OF LOG RHOS

$X_0$	$X_1$	$X_2$
-0.162668E + 6	0.410074E + 1	-0.288224E + 8
$X_3$	$X_4$	
0.815834E + 8	-0.774802E + 8	

THE FOLLOWING ARE COMPUTED VALUES OF RHO

X	RHOS	DERIVE	RHO
-	-	-	-
-	-	-	-
-	-	-	-

This table was given for 900°C case, in the model  
evaluation; Chapter 5.

'DIFCOF' is package which organises the computations of diffusion coefficient. It makes use of routine 'COMPUT'. The values of  $X_1$ ,  $X_2$ ,  $T$ ,  $C_{AXT}$ ,  $C_{BXT}$ ,  $K$ ,  $\text{ALPHA}$ ,  $CS$  are all available for 'COMPUT'. In addition 'COMPUT' has 4 parameters  $I$ ,  $J$ ,  $DA$ , and  $DF$ .  $DA$  is the value of  $D_A$  in the equation,

$$\frac{2}{(1-K)} \frac{C_A(x, t)}{\left[ C_S \left( 2 - \operatorname{erf} \frac{x-\alpha t}{2\sqrt{D_A t}} - \operatorname{erf} \frac{x-3\alpha t}{2\sqrt{D_A t}} \right) \right]} = e^{-\frac{\alpha(x-\alpha t)}{2 D_A}}$$

When  $J = 0$ , the routine makes use of the above equation and using  $C_{AXT}$  if  $I = 1$ , or  $C_{BXT}$  if  $I = 2$ , computes the L.H.S. and R.H.S. of the above equation.  $DF$  is set to the difference between the LHS and RHS. When  $J = 1$  the routine computes the values of  $C_{AXT}$  ( $I = 1$ ) or  $C_{BXT}$  ( $I = 2$ ) and  $DF$  is set to that value.

'DIFCOF' takes in the values of  $X$ ,  $T$ ,  $C_{AXT}$ ,  $C_{BXT}$ ,  $K$ ,  $\text{ALPHA}$ ,  $CS$ ,  $R_{MAX}$ ,  $R_{MIN}$  as input.  $R_{MAX}$  and  $R_{MIN}$  are the range of values between which  $DA$  lies. By repeatedly making use of the routine 'COMPUT' with appropriate control parameters, the  $DA$  is set to  $R_{MIN}$ ,  $R_{MAX}$  and  $(R_{MAX} + R_{MIN})/2$  and the differences between the LHS and RHS of the above equation are computed. As the value of LHS-RHS is monotonically

decreasing logarithmic search is made to find the value of DA which satisfies the equation. Everytime the difference is computed at the middle point of RMAX and RMIN and if the difference is positive RMAX is set to the average; if the difference is negative RMIN is set to the average. Then the procedure is repeated with the new values of RMAX and RMIN. This continues until the difference between the LHS and RHS is  $0.1E + 8$ . The value of DA at this point is given as the accurate value. Similary DB is computed.

Using the values of DA and DE and the given values of X, the values of CAXT, CBST, and CX are computed by using the routine 'COMPUT' in the J = 1 mode. The results are tabulated.

Typical input to and output of the package are shown below: -

Input given  $X_1$ ,  $X_2$ , CAXT, CBXT, T, K, ALPHA, CS, RMAX, RMIN and the values of X are

.12E-4, .40E-4, .25E+20, .30E+19, 3600.0, 0.1, 0.222E-8,  
0.30E+21, 0.10E-9, 0.10E-16

The output is as follows:

#### CALCULATION OF DA:

RMAX = 0.100000E-9, RMIN = 0.100000E-16, R = 0.500000E-10,  
DF = -0.906822E00  
RMAX = 0.500000E-10, RMIN = 0.100000E-16, R = 0.250000E-10,  
DF = -0.906527E00

-----  
-----

RMAX = 0.187007E-14, RMIN = 0.187006E-14, R = 0.187007E-14,  
DF = -0.242144E-7

THE VALUE OF DA SATISFYING THE GIVEN EQUATION IS FOUND TO BE  
0.187007E - 14.

Similarly DB also can be found out.

THE FOLLOWING ARE COMPUTED VALUES

X	CAXT	CBXT	CX
-	-	-	-
-	-	-	-
-	-	-	-

Tabulation of those values for 900°C diffusion has  
shown in the model evaluation, Chapter 5.

ALL ROUTINES ARE WRITTEN IN FORTRAN IV. 'BULKR' is  
a 200 statement program and its average execution time is about  
2 seconds for a problem 'DIFCOP' is an 80 statement program  
and its average time of execution is 2 seconds.

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